

Appendix A

12 ORGANOSILANES: WHERE TO FIND THEM, WHAT TO CALL THEM, HOW TO DETECT THEM

may also be referred to as siliconates). Silicates, of course, are also the salts of silicic acid $[\text{Si}(\text{OH})_4]$. The structure of the extracoordinate (5- versus 6-) compounds is obvious from the number of substituents contained in the name. For pentacoordinate compounds, which typically form trigonal bipyramidal structures, one must further label the equatorial and axial substituents.

Reactive Silicon Species: Many of the exciting developments in organosilicon chemistry have arisen from the preparation of stable versions of normally reactive silicon-based intermediates. The nomenclature commonly used for reactive intermediates may be found in Table 1.2. The prefix “*sila*” implies a carbon compound with silicon replacing a carbon, rather than a carbon compound containing a pendant silyl group. For instance, silaethylene (silaethene) is $\text{H}_2\text{Si}=\text{CH}_2$; silylethylene (silylethene) is $\text{H}_3\text{SiHC}=\text{CH}_2$.

1.3.6. Organic versus Organosilicon Nomenclature

The usage of nomenclature for organosilanes is often tempered by the perspective of the scientist. The subset of scientists who think of themselves as “silicon chemists” tend to use the silane nomenclature, with the organic residue demoted to substituent status. On the other hand, organic chemists typically focus on the organic skeleton and see the silyl group as another heteroatom-based substituent. The proper nomenclature for silicon-containing radicals, when appended to an organic structure, is shown in Table 1.3.

1.3.7. Silicones: General Electric Siloxane Notation

The basic building blocks produced by the silicone industry are functional, methylated silanes that are then hydrolyzed to give siloxanes (see Chapter 9). In order to facilitate the description of these compounds, the presence of methyl groups is assumed unless otherwise specified. Silicone components are differentiated by the number of oxygen attachments (M = monofunctional, D = difunctional, etc.). The combination of these terms allows the facile description of a complex silicone polymer structure (Chart 1–2). In cases where a methyl

Table 1.2. Nomenclature for Silicon-Based Reactive Intermediates and Relatively Unstable Compounds

Reactive intermediate	Nomenclature
R_2Si :	silylene (carbene analogue)
R_3Si^+	silylium ion (silacinium ion, silicon cation)
$\text{R}_3\text{Si}^\bullet$	silyl radical
R_3Si^-	silyl anion
$\text{R}_2\text{C}=\text{SiR}'_2$	silene (alkene analogue)
$\text{R}_2\text{Si}=\text{SiR}'_2$	disilene (alkene analogue)
$\text{R}_2\text{Si}=\text{O}$	silanone (ketone analogue)
$\text{R}_2\text{Si}=\text{NR}'$	silanimine (imine analogue)

Table 1.3. Silicon-Based Radical Names

Structure	Name
H ₃ Si—	silyl
H ₃ Si—SiH ₂ —	disilanyl
H ₃ Si—O—	siloxo
H ₃ Si—S—	silylthio
H ₃ Si—NH—	silylamino
H ₃ Si—O—SiH ₂ —	disiloxanyl
H ₃ Si—O—SiH ₂ —O—	disiloxanoxy
Me ₃ Si	trimethylsilyl

Adapted from Ref. 13, with permission. Copyright Colin Eaborn.

group is replaced by a different residue, this is indicated by a superscripted symbol. Thus D^H represents $\sim OSiMeH \sim$, M^{Ph} represents $\sim OSiMe_2Ph \sim$. For instance, **1-1** is D_3D^H (Chart 1-3).

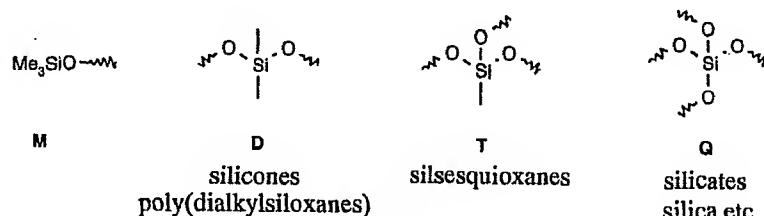


Chart 1-2

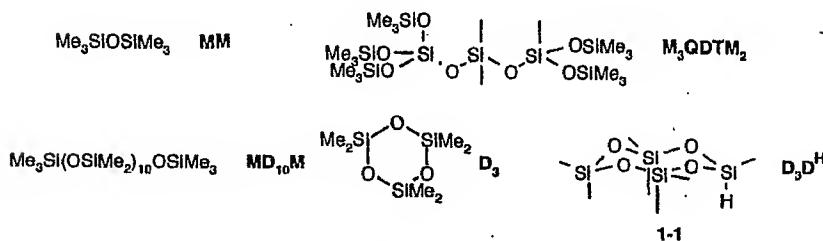


Chart 1-3

1.4. NMR CHARACTERIZATION OF SILICON-CONTAINING SPECIES

A description of the available spectroscopic (e.g., infrared), spectrometric (e.g., mass spectrometry), and wet analytical techniques for the characterization of silicon-containing compounds is beautifully described in the authoritative review edited by Smith.¹⁵ The most important of these techniques in the author's view is nuclear magnetic resonance (NMR) for: (1) its simplicity;